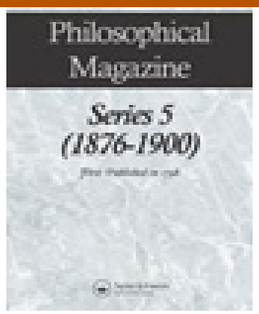

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LVIII. On the thermal phenomena of the galvanic pile, and electromotive forces

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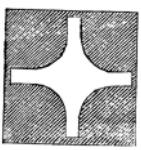
The outer tube being filled with water, the bar of copper heated to a dark red is placed in the inner tube, the cap adjusted, and a rock-salt plate $\frac{1}{20}$ of an inch thick shaped thus

placed on the to pof the cap, the blotting-paper with its waxed surface downwards brought immediately over but not touching the salt: the heat ascending melts the wax, and a well-defined outline of the rock-salt plate is produced on the upper surface of the blotting-paper, thus



If the experiment be performed without the rock-salt plate, the melted wax first shows itself as a dark spot in the centre of the blotting-paper, and then spreads towards the edges. Different shaped plates were used with similar results. In performing the experiment care must be taken that the heated copper stands fairly perpendicular under the centre of the cap.

LVIII. *On the Thermal Phenomena of the Galvanic Pile, and Electromotive Forces.* *By* E. Edlund*.

§ I.

1. From the experiments which have been instituted for the purpose of studying the thermal phenomena of the galvanic pile and its conductors the conclusion has been drawn, that the heat which arises in consequence of the passage of the current through the entire conduction (including the pile itself) during a certain time is exactly equal in quantity to that which is produced in the pile by chemical processes during the same time,—that is to say, provided that the current performs no external work (for example, induction, chemical decomposition, &c.); and among the processes mentioned, only those must be understood which are primary and in direct connexion with the formation of the current. In the following, to distinguish these two quantities of heat from one another, we will name that which is occasioned by the passage of the current through the conductors the gal-

* Translated from a separate impression, communicated by the Author from Poggendorff's *Annalen*, vol. clix. pp. 420–456.

vanic, and that which arises from the chemical processes in the pile the chemical heat. Then it has been inferred, from the experiments which have been made, that, under the presupposition mentioned, the chemical is equal in amount to the galvanic heat. Calling the galvanic heat gw, according to Joule's law $gw = Mi^2lt$, where M is a constant, i denotes the current-intensity, l the resistance of the conduction and the pile together, and t the time during which the current is in action. Therefore, if E denotes the electromotive force of the pile, we can also write $gw = MEit$, from which, in consequence of the inference drawn, we obtain $kw = MEit$, if kw signifies the heat evolved by the primary chemical processes in the pile. If n denotes the number of chemical equivalents decomposed by the action of the current at the positive-pole plate of the pile, according to the law of electrolysis $n = mit$, m denoting a constant which is independent of the nature of the electrolytic liquid. Hence we conclude that $kw = \frac{Mn}{m}E$, and therefore that, for one equivalent, $kw = \frac{M}{m}E$, from which it follows that the quantity of heat which is produced in the pile by the primary chemical processes while one equivalent is decomposed at the positive pole is a measure of the electromotive force of the pile.

If the galvanic is in reality precisely as great as the primary chemical heat, we may consequently say that the whole efficacy of the current consists only in this, that it conducts the chemical heat to all parts of the closed circuit, and deposits at each place exactly as much as corresponds to the resistance at the same place—although of course it is very difficult to form a clear conception of the actual physical processes that take place in this conduction. If by direct measurement of the heat produced in the pile itself it were to be found that its amount is greater than that of the galvanic heat occasioned by the passage of the current, or, in other words, exceeds the heat which the current calls forth in a metallic conductor whose resistance is equal to that of the pile, we should have to admit that this excess was derived from the secondary processes which may take place in the pile and have nothing in common with the formation of the current. In this way also it has been attempted to explain such surplus heat in the cases in which it has been observed:—If a chemical-decomposition cell or a voltameter be inserted in the circuit, so that the current has opportunity to decompose water, for example between platinum poles, then, according to the way of regarding it now presented, all the primary chemical heat

arising in the pile cannot pass over into galvanic heat, but a part of it is expended for the mechanical work necessary for generating the electromotive forces of polarization and the chemical decomposition in the cell. We can imagine this brought about by the store of chemical heat requisite for this work being carried by the current from the pile into the decomposition-cell, where it is employed for the purpose mentioned. Consequently no other change of temperature can arise in the decomposition-cell than that which is occasioned by the passage of the current through the electrolytic liquid. The heat generated in the decomposition-cell must therefore be equal to that which is produced when the current passes through a metallic conductor the resistance of which is equal to that of the liquid. Now, as by direct measurement the quantity of heat produced in the decomposition-cell has been found greater than the galvanic, the cause of this has been sought in the secondary chemical processes which may take place there and are independent of the current.

2. I have already, some years since *, given another explanation of the thermal phenomena in question. It was, in brief, the following:—If the current does no external work, its total action consists in calling forth heat in the conductor through which it passes. After the current has ceased, no other products of the activity of the pile are found but the chemical changes in the pile and the heat which has arisen, partly in the pile itself, and partly in the conductors. It is evident, however, that the amount of this heat must be equivalent to the chemical changes; that is, in other words, the quantity of heat generated must be exactly equal to that which would have resulted from the same chemical changes if no current had taken place; for otherwise either chemical work or heat would have been obtained out of nothing. The current has therefore, upon the whole, generated no heat at all; its total heat-production is equal to *nil*. But we know that the current does a certain amount of mechanical work in order to overcome the resistance of the galvanic conduction; and this work changes into heat. Therefore the current brings forth in the conduction an actual production of heat. But, because the total heat-production of the current must be equal to *nil*, this can only happen through a consumption of heat occurring at some place or other in the conduction; and of course the place can be no other than that where the electromotive force has its seat. We consequently arrive at the result that, in order to produce the cur-

* *Öfversigt af K. Vetenskaps Akademiens Förhandlingar*, 1869; Pogg. *Ann.* vol. cxxxvii. p. 174.

rent, the electromotive force consumes a quantity of heat exactly equal to the quantity generated by the current in overcoming the resistance of the galvanic conduction. The heat-consumption of the electromotive force is accordingly equal to gw; yet it does not hence follow that it is not also equal to kw, or that gw and kw have not the same magnitude.

If only a single electromotor is inserted in the closed circuit, keeping the same notation as before, we have

$$gw = \mathrm{M}i^2lt = \mathrm{ME}it;$$

therefore in unit time a quantity of heat is consumed which is proportional to the product of the electromotive force and the intensity of the current. Thus, during the solution of one equivalent of zinc, the total amount of heat gw consumed by the electromotor $= \frac{\mathrm{M}}{m}\mathrm{E}$. This holds, even if l be changed—that is, even if the current-intensity be increased or diminished. Are two electromotors E and E′ acting in the same direction? then in unit time the total heat-consumption in both must be $\mathrm{M}(\mathrm{E}+\mathrm{E}')i_{,,}$, if $i_{,}$ denotes the intensity of the current produced; hence, evidently, $\mathrm{ME}i_{,}$ is consumed in the former, and $\mathrm{ME}'i_{,}$ in the latter. When E is greater than E′ and the one electromotor acts in the opposite direction against the other, the total quantity of heat consumed becomes $\mathrm{M}(\mathrm{E}-\mathrm{E}')i_{,,,}$, if $i_{,,}$ denotes the current-intensity. In the first electromotor the quantity $\mathrm{ME}i_{,}$ of heat is now consumed; but this is greater than the total quantity generated by the current in consequence of the galvanic resistance. In the other electromotor, therefore, a quantity of heat equal to $\mathrm{ME}'i_{,,}$ must be generated. Consequently, when the current traverses the electromotor in the same direction in which the electromotive force acts, a quantity of heat is consumed which is proportional to the product of the electromotive force and the current-intensity; but if the current goes in the contrary direction, just as great a quantity of heat is produced instead*.

From this it is evident that these two ways of considering the subject agree in one respect, namely that, according to both, the sum of the heat which the current produces upon the whole is equal to *nil*; but in the one case the heat produced in the pile by the chemical processes is regarded as conveyed to the different parts of the circuit; while in the other heat is supposed to be generated by the current everywhere in the circuit; yet the total quantity of heat produced is equal

* The unitarian view of the nature of electricity leads direct to the same result. See "Théorie des phénomènes électriques," p. 45 (*K. Vetenskaps Ak. Handl.* Bd. xii. No. 8: also Brockhaus, Leipzig).

to that which is consumed by the electromotive force. In other respects the two views lead to divergent results: for example, according to one view the quantity of the primary chemical heat is equal to that of the galvanic, wherefore the former also gives a measure of the electromotive force; according to the other these two quantities may be different, and consequently the primary chemical heat cannot serve as a measure for the electromotive force, &c.

In order to determine which of these two views accords best with experience, we will more closely consider the experiments which have been instituted for the purpose of studying the thermal phenomena of the pile and of the current. For brevity, we will name the first-cited method of consideration No 1, and that proposed by me No. 2.

3. Favre * has endeavoured, by direct experiments, to answer the question, Is the whole of the galvanic heat which arises in the circuit derived merely from that which is generated by the chemical processes? For this he made use of a mercury calorimeter with two muffles situated close to one another, of the same nature as the calorimeter which Favre and Silbermann had previously employed in their determinations of the heat developed in chemical processes. The pile he used consisted of a glass tube filled with water containing sulphuric acid, in which were placed the two pole-plates, amalgamated zinc and platinized copper (Smee's pile). It was closed with a fine platinum wire, which was of unequal length and thickness in different experiments. The hydrogen evolved in the pile was collected and measured. The experiment was first made in this way:—The pile was enclosed in one muffle, and the platinum wire in the other; at the same time it must be remarked that the copper wires connecting the pole-plates with the ends of the platinum wire, and which were outside of the calorimeter, were so thick that no perceptible development of heat could take place in them. When, therefore, the experiment was thus arranged, the calorimeter indicated the total sum of the heat which was developed in the pile and the entire circuit while the current was in action; and since the quantity of the hydrogen gas developed was at the same time known, it was easy to calculate what the sum of the heat would have been if the experiment had been continued until one equivalent of zinc in the pile was dissolved. Thereupon the experiment was varied by leaving the platinum wire outside of the calorimeter, in consequence of which the galvanic heat which arose in the wire had no effect upon the calorimeter. The

* *Annales de Chimie et de Physique*, (2) t. xl. p. 293 (1854).

difference between the indications of the calorimeter in the two cases was consequently equal to the galvanic heat which was developed in the platinum wire. The results of the different experiments will be seen from the following Table. Column *a* gives the length of the wire ; *b*, the deflection of the calorimeter in heat-units (the gram being taken as unit of weight) when both the pile and the platinum wire were enclosed in the calorimeter ; *c*, the corresponding deflection when the platinum wire was excluded from the calorimeter ; $b-c$, the difference between these two deflections, or the galvanic heat developed in the wire ; and *gw* the quantity, thence obtained by calculation, of the galvanic heat in the pile and the platinum wire together.

Diameter of the wire =0·265 millim.

a.	*b*.	*c*.	$b-c$.	*gw*.
millim.				
25	18092	13127	4965	9652
50	18247	11690	6557	
100	18185	10439	7746	10820
200	18022	8992	9030	

In another series of experiments, in which a thinner wire was used, the following results were obtained :—

Diameter of the wire =0·175 millim.

a.	*b*.	*c*.	$b-c$.	*gw*.
millim.				
50	18082	9955	8127	12040
50	18173	10101	8072	
100	18066	8381	9685	
Mean ...	18124	.....	.....	10837

As the preceding Tables show, the value of *gw* increases as the resistance becomes greater and therefore the current-intensity less.

According to Favre and Silbermann, there are developed,

	Heat-units.	
in the combination of one equivalent of zinc (33 grams) with oxygen . .	42451	
in the combination of the oxide with sulphuric acid	10455	
On the other hand, in the decomposition of one equivalent of water,	34462	are consumed.
Sum . .	18444	

The mean, 18124, of the numbers found in the above experiments differs only about 300 heat-units from the last-mentioned sum; wherefore the two may be regarded as equal. But according to both views, No. 1 and No. 2, this equality must exist; and so we have no clue to enable us to judge in what way the galvanic current is produced; whether we take No. 1 or No. 2 as the correct way of considering, in this respect we come to the same result. The calculation of the quantity of galvanic heat developed by the current in the entire circuit (a calculation not carried out by Favre in these experiments) shows that it amounts on the average to 10837 thermal units, not much more than the half of the chemical heat.

The circumstance that, as results from the above experiments, the galvanic heat gw developed by the current in the entire circuit increases when the resistance is increased and consequently the current-intensity is diminished, is confirmed by Favre's later experiments with Smee's pile *. In one of these experiments, the length of the platinum wire being shortened from 7000 to 250 millims., the galvanic heat was lessened from 18018 to 14424 thermal units; the chemical heat he found somewhat greater than before, namely 19834 units. While the chemical heat, as we know beforehand, is constant and independent of the inserted resistance, the galvanic heat, on the contrary, became less when the resistance was diminished and consequently the intensity of the current was augmented. In all these experiments, however, the chemical was greater than the galvanic heat.

In the following experiments, on the contrary, the galvanic exceeded the chemical heat; for there appeared in the pile an actual consumption of heat, so that its temperature sank on the passing of the current, instead of rising †. One of the pole-disks of the pile employed consisted of platinum, the other of zinc or cadmium; and both were immersed in hydrochloric acid. The closed pile was first put into the calorimeter without any exterior resistance, by which a measure of the total chemical heat was obtained. Afterwards the pile was furnished with a considerable exterior resistance and then enclosed in the calorimeter, but so that the resistance was left outside. The chemical heat amounted, for the cadmium-platinum pile, to 7968 units, and for the zinc-platinum pile to 15899; but when the resistance was left outside of the calorimeter, there was observed, in the cadmium-platinum pile, a

* *Comptes Rendus*, t. xlvii. p. 599 (1858), and t. lxvii. p. 1012 (1868).
† Ibid. t. lxviii. p. 1300 (1869).

lowering of temperature 1288, and, in the zinc-platinum pile, 1051 thermal units.

Favre * has also, with the aid of the mercury calorimeter, determined how much chemical and galvanic heat is liberated in some piles of another construction during the solution of one equivalent of zinc †.

We will here take into consideration only the numerical values obtained by Favre for the piles of Daniell and Grove. If *kw* denote all the chemical, and *gw* all the galvanic heat, he obtained for Daniell's pile $kw=25060$, $gw=23993$, and consequently $kw-gw=1067$ thermal units; for Grove's pile $kw=41490$, $gw=46447$, and consequently $kw-gw=-4957$ units; so that in Daniell's pile the chemical heat is only about 1000 units greater than the galvanic, while in Grove's pile the galvanic is greater than the chemical heat. Consequently, when this pile is closed with a conducting wire of great resistance, the pile itself is cooled during the passage of the current, while the conducting wire is heated.

We may add that Raoult also has determined by direct ex-

* *Comptes Rendus*, t. lxix. p. 34.

† The following was the method of observation here employed:—The pile to be investigated was enclosed in one muffle of the calorimeter. As the progress of the chemical processes could be determined with great accuracy by measuring the hydrogen which was evolved in the Smee's pile, such a pile was also placed in the calorimeter, and connected with the other pile, so that the current passed through both. The rheostat, which connected the two poles, was also enclosed in the calorimeter. Thus the calorimeter gave the chemical heat developed in both piles. The quantity of heat shown by the calorimeter while half an equivalent of hydrogen was being evolved in the Smee pile was now observed—that is, during the time that the chemical processes in the two piles together corresponded to one equivalent. When a Daniell's and a Smee's pile were placed in the calorimeter, 22447 heat-units were in this way obtained. The quantity of chemical heat for one equivalent of hydrogen, in the Smee's pile employed, was determined, by special trial, at 19834 thermal units, or 9917 for a half-equivalent. Consequently, if the quantity of chemical heat corresponding to 1 equivalent for the Daniell's pile be called x, we shall have

$$\frac{x}{2}+9917=22447, \text{ whence } x=25060.$$

A fresh experiment was then made, in which the Smee's pile and the rheostat resistance were taken out of the calorimeter, so that the Daniell's pile alone remained within. The outer resistance was so great, that the heating caused by the current in consequence of the resistance in the pile itself could be neglected. With this arrangement, the calorimeter now gave the difference between the chemical and the galvanic heat, or $gk-gw$. In this way was obtained, during the evolution of one equivalent of hydrogen in the Smee pile, $gk-gw=1067$ thermal units. Subtracting this number from 25060, we get 23993, which denotes the galvanic heat of the Daniell pile. Favre proceeded in the same manner in his investigation of the other piles.

periments the galvanic heat of Daniell's pile, and found that it amounts to 23900 thermal units, which agrees closely with M. Favre's result*.

If the difference which is almost always found between the quantities of the chemical and the galvanic heat is caused by the secondary chemical processes which may take place in the pile, we must assume, in accordance with what has been said above, that these processes bring forth in some piles a production, in others a consumption of heat. Favre thought at first that the galvanic heat was exactly equal in quantity to the chemical†. Subsequently he shared the view already expressed by others, that the cause of the difference in question in Smee's pile lay in this, that the hydrogen at the negative platinum disk was separated in the active state, or *in statu nascenti*. As afterwards the hydrogen leaves the platinum disk and escapes upward through the liquid, it passes over into its ordinary condition, in which process heat is liberated, which probably raises the temperature of the liquid, but does not augment the electromotive force‡. But the unexpected relation shown by the cadmium-platinum and zinc-platinum piles charged with hydrochloric acid finally convinced him that this also could not be the true explanation §.

In order, therefore, to explain the difference in the ordinary Smee's pile, we must assume that heat is evolved on the transition of the hydrogen from the active to the ordinary state, and that this heat merely raises the temperature of the liquid in the pile, without affecting the electromotive force. In the two piles last mentioned, with hydrochloric acid as the liquid, hydrogen separates *in statu nascenti* upon the negative platinum disk; but here, in order to account for the difference in question, we must assume that cold is generated when the hydrogen passes from the above-mentioned state into its ordinary condition—an assumption which contradicts the preceding one. Favre, on this account, ascribes this fact to other, secondary chemical processes which may occur in the pile; but he does not specify in what those processes are to consist. The fact that the galvanic heat which is developed in Smee's pile by the current increases with the inserted resistance, Favre has endeavoured to explain by assuming that the ratio between the primary and secondary processes is, as to its magnitude, dependent on the intensity of the current.

* *Ann. de Chim. et de Phys.* [4] t. iv. p. 392 (1865).

† Ibid. [3] t. xl. (1854).

‡ *Comptes Rendus*, t. lxvii. p. 1012 (1868). Compare with this Bosscha's investigation in Pogg. *Ann.* vol. ciii. (1858).

§ Ibid. t. lxviii p. 1300 (1869).

From the foregoing it follows without doubt that it is very difficult to employ the mode of representation No. 1 for the explanation of the thermal phenomena which take place in the galvanic pile and its circuit. Even if we leave out of consideration that it is by no means easy to understand in what manner the heat is conveyed from the pile to the different conductors outside of it, it may yet be truly said that it has been attempted to attribute the difference between the amounts of the chemical and the galvanic heat to causes whose presence cannot with any certainty be proved, and the actions of which are still less determined quantitatively. It appears to me that such a way of explaining cannot, from a scientific point of view, be called a good one. The question takes another form when representation No. 2 is employed. The assumption that the electromotive force expends a certain quantity of *vis viva* or heat to produce the work of the current is fully justified, because it is valid also for forces different in nature from the electromotive. That the consumption of heat by the electromotive force must be equal to the production of heat by the current is self-evident; yet it does not by any means necessarily follow that this heat-consumption is exactly equal to the quantity of heat which is generated by the chemical processes in the pile.

Employing representation No. 2, the experiments cited in the foregoing show that the heat-consumption occasioned by the electromotive force in the zinc-platinum and cadmium-platinum piles with hydrochloric acid for the electrolytic liquid, is greater than the heat-production brought about by the chemical processes which take place in these piles, but that the ratio in the Smee pile is inverse. It is easy to understand that the consumption of heat, and consequently also the quantity of galvanic heat in the entire circuit, in the Smee pile, must be less when the external resistance is diminished. The negative platinum disk in this pile is polarized by hydrogen; and when currents so feeble as those which occur in these experiments are in question, the polarization increases with the intensity of the current. Therefore, when the external resistance is little, the electromotive force of the polarization must be relatively great, and consequently the total electromotive force of the pile become inconsiderable. It is therefore evident that the heat-consumption of this force, and consequently also the galvanic heat developed by the current, must diminish with the resistance. We have therefore no need to have recourse to unknown causes in order to account for the results obtained by the experiments instituted.

4. For determining indubitably which of the two repre-

sentations, No. 1 or No. 2, deserves to be preferred, we obtain the best clue from the experiments instituted in order to measure the heat-phenomena in a chemical-decomposition cell or voltameter. With this view Raoult employed partly water acidulated with sulphuric acid, and partly a solution of sulphate of copper as electrolytic liquid, and with the help of a mercury calorimeter measured the quantity of heat which arose in the decomposition-cell over and above the quantity occasioned there by the passage of the current in consequence of the resistance*. If W is the total heat developed in the voltameter, and gw (as before) the heat which the passage of the current occasions in consequence of the resistance (or the galvanic heat), $W-gw$ was measured. This heat-difference, which Raoult calls the local heat, may in the following be denoted by L. By special experiments Raoult moreover measured the polarization-electromotive force produced in the voltameter during the passage of the current. This electromotive force may be denoted by e, and that of an element of the Daniell pile by d. The series employed consisted, in the different experiments, of from two to twelve Daniell elements. The numbers cited below under L denote the number of heat-units which were developed in the voltameter during the liberation of one equivalent of hydrogen or copper. As, moreover, it cannot be necessary to describe more closely the arrangements in the experiments, we may here add only that, with the decomposition of the sulphuric-acid water, the two poles in the voltameter consisted of platinum wires in the first two experiments (A and B)—while in the third experiment (C) only the positive pole consisted of platinum, the negative being formed of a thick wire of copper. In all three experiments with the copper solution the positive pole consisted of a thick wire of platinum, and the negative of one of copper. As may readily be understood, the voltameter alone was enclosed in the calorimeter, and the piles stood outside of it.

The following were the results obtained :—

On the decomposition of the water.		On the decomposition of the sulphate of copper.	
$\frac{e}{d}$.	L.	$\frac{e}{d}$.	L.
A. 2·04	+14898	A. 1·59	+7594
B. 1·75	+ 7596	B. 1·58	+7997
C. 2·16	+17626	C. 1·36	+2821

From this we see that in both cases a considerably greater

* *Ann. de Chim. et de Phys.* [4] t. iv. p. 411; see also t. ii. p. 317.

quantity of heat is produced than the galvanic which is caused in the voltameter by the passage of the current; and this happens notwithstanding it might be supposed, in consequence of the chemical decomposition of the liquid, that the result would be a cooling.

Raoult is of opinion that the cause of the heating in this case is to be sought in secondary chemical processes occurring in the voltameter, which have nothing to do with the current. He supposes that the constituents of the electrolyte, which cover the electrodes and cause the polarization, are easily decomposable, and on their decomposition give rise to a heat-production in the same manner as takes place with the hyperoxide of hydrogen—that the decomposition of these products first takes place after they have left the electrodes and begin to ascend through the liquid, in consequence of which this is heated by them without the current being at all affected. In my view, this explanation is unsatisfactory; on the other hand, heat-production is in this case a necessary consequence if we start from representation No. 2.

According to this way of representing it, if a current passes through an electromotor in the direction required by its electromotive force, a quantity of heat is consumed which is proportional to the electromotive force, multiplied by the intensity of the current; but if the current goes in the opposite direction, just as great a quantity of heat is generated. If, therefore, the current is permitted to traverse the electromotor during so long a time that an equivalent of the electrolyte is decomposed, the quantities of heat consumed or generated become proportional to the electromotive force. Consequently there arises in the voltameter a source of heat, because the electromotive force of the polarization acts in the opposite direction against the current which is passing through. It has been mentioned above that the galvanic heat-development in a closed Daniell pile during the liberation of an equivalent of copper amounts to 23900 heat-units; and according to No. 2, exactly so much heat must, during the same time, be consumed by the electromotive force of the pile. With the help of this datum it is easy to calculate the magnitude of the above-mentioned source of heat in the various experiments instituted by Raoult; for we need only multiply $\frac{e}{d}$ with the last-mentioned number. But, moreover, heat is consumed by the chemical decomposition in the voltameter. For each equivalent, 34462 thermal units are consumed, according to Favre and Silbermann, in the decomposition of the water; and, according to Raoult, 29605 in the decomposition of the

salt of copper. If from the quantity of heat developed by the electromotive counterforce the last-mentioned quantity of heat, consumed by the decomposition, be subtracted, we actually obtain, as the following Table shows, the values observed by Raoult of the surplus heat L.

In the decomposition of water.

		L.
A	$(2{\cdot}04 \times 23900)$.	$48756 - 34462 = +14294$
B	„ „	$41825 - 34462 = +\ 7363$
C	„ „	$51624 - 34462 = +17162$

In the decomposition of sulphate of copper.

		L.
A	$(1{\cdot}59 \times 23900)$.	$38001 - 29605 = +8396$
B	„ „	$37762 - 29605 = +8157$
C	„ „	$32504 - 29605 = +2899$

Indeed the calculated do not differ more from the observed numbers than can be accounted for from the unavoidable errors of observation occurring in experiments of this sort. Hence it follows that, to account for the thermal phenomena occurring in the voltameter, there is no need to have recourse to the secondary chemical processes which may take place there, the nature and amount of which are more or less unknown*; the theoretical view above presented under No. 2 perfectly suffices for their explanation.

5. Some experiments made by Favre, on the development of heat in the voltameter, fully confirm what is here alleged †. In a mercury calorimeter (No. 1) provided with seven muffles, in the first five muffles five equal Smee's elements were enclosed, and in the sixth a rheostat consisting of a platinum wire with so great a resistance that the resistance of the remaining parts of the circuit, in comparison with it, could almost be neglected. On the solution of one equivalent of zinc in each element, the calorimeter indicated the quantity of chemical heat k developed in the five elements.

* Raoult, in order to show that the occurrence of secondary chemical processes is necessary for the production of the heat in this case, makes an inference which might be rendered in the following manner:—When the voltameter is inserted in the circuit, the electromotive force of the series is thereby diminished by e, and the entire circuit is thus deprived of a quantity of heat which is equal to $23900 \times \frac{e}{d}$. This heat is expended in the production of chemical decomposition in the voltameter. But as the quantity of heat expended for this is less than that above-mentioned, the difference must be made good by the occurrence of secondary chemical processes.

† *Comptes Rendus*, t. lxvi. p. 252; Pogg. *Ann.* vol. cxxxv. p. 300 (1868).

The same experiment was then repeated, with only this difference, that a voltameter was enclosed in the seventh muffle. In this the quantity of heat $k-a$ was obtained, where a (as shall presently be shown) denotes the quantity of heat which was consumed in the chemical decomposition of the electrolyte in the voltameter. In this way Favre found, as the equivalent for the chemical decomposition of water, 34204, and for the decomposition of sulphate of copper 26568 thermal units.

Thereupon the following experiments were made:—The voltameter was taken out of the calorimeter No. 1, and placed in another calorimeter, No. 2; while the series and rheostat remained in No. 1. It was now found that calorimeter No. 1 indicated, on the electrolysis of water, 54235 heat-units less than in the first experiment—that is, when the series and rheostat were enclosed in No. 1 and no voltameter was inserted in the circuit. When the voltameter contained the copper-solution, 38530 units of heat less than in the first experiment were obtained in the same calorimeter. The calorimeter No. 2 gave, in the former case, a heating of 20335, and, in the latter, one of 12445 units.

Upon this Favre asks, What can be the reason that the large quantity of heat that has disappeared in the series is again found in the calorimeter No. 2? This cause, he continues, cannot be referred to the physical resistance of the voltameter; for this is so insignificant that it might almost be neglected in comparison with the resistance of the rheostat. According to his view the cause is to be sought in the circumstance that the substances which take part in the chemical processes (oxygen, hydrogen, &c.) are found now *in statu nascenti*, now in the ordinary state. This explanation appears to me quite unsatisfactory. Even if it be assumed that such secondary chemical processes take place in the voltameter, they can certainly cause a heating of the voltameter, but they cannot possibly account for the great loss of heat which takes place in the series and rheostat.

[To be continued.]

LIX. *Mode of the Propagation of Sound, and the Physical Condition determining its Velocity on the Basis of the Kinetic Theory of Gases.* *By* S. Tolver Preston *.

1. SINCE the kinetic theory of gases is now generally accepted by physicists, affording, as it does, a rational explanation of the physical qualities and deportment of gases

* Communicated by Professor Clerk Maxwell.